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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

U.S. Patent Application For

**ATTACHMENT OF ORGANIC MOLECULES TO GROUP
III, IV, OR V SUBSTRATES**

Inventor(s): **DAVID F. BOCIAN**, a citizen of the United States of America,
residing at 6308 Glen Aire Avenue, Riverside, CA 92506, USA
JONATHAN S. LINDSEY, a citizen of the United States of
America, residing at 3931 Napa Valley Drive, Raleigh, NC 27612
ZHIMING LIU,
AMIR A. YASSERI
ROBERT S. LOEWE

Assignee: **The Regents of the University of California**
Entity: **Small Entity**

**QUINE INTELLECTUAL PROPERTY LAW
GROUP P.C.**
2033 Clement Ave
Alameda, CA 94501
Tel: (510) 337-7871
Fax: (510) 337-7877

ATTACHMENT OF ORGANIC MOLECULES TO GROUP III, IV, OR V SUBSTRATES

CROSS-REFERENCE TO RELATED APPLICATIONS

5 [0001] This application claims priority to and benefit of USSN __/____,____, filed on July 25, 2003, entitled ATTACHMENT OF ORGANIC MOLECULES TO GROUP III, IV, OR V SUBSTRATES, and naming DAVID F. BOCIAN, JONATHAN S. LINDSEY, ZHIMING LIU, AMIR A. YASSERI, and ROBERT S. LOEWE as inventors, which is incorporated herein by reference in its entirety for all purposes.

STATEMENT AS TO RIGHTS TO INVENTIONS MADE UNDER FEDERALLY 10 SPONSORED RESEARCH AND DEVELOPMENT

[0002] This invention was made with Government support under Grant No. MDA972-01-C-0072 awarded by the Army. The Government has certain rights in this invention.

FIELD OF THE INVENTION

15 [0003] This invention pertains to the field of semiconductor fabrication. In particular this invention provides novel methods of coupling organic molecules to group III, IV, and V elements (*e.g.*, silicon, germanium, *etc.*), and the like.

BACKGROUND OF THE INVENTION

20 [0004] The fabrication of ordered molecular assemblies on conducting silicon surfaces is of considerable interest owing to its potential applications in the microelectronic industry. One goal of semiconductor fabrication is to increase the density of active elements provided on an integrated circuit. In order to accomplish this, efforts have turned to the use of self-assembling molecular structures as an alternative to, or in conjunction with various lithographic processes to form the active elements used in integrated circuits.

25 [0005] In addition, interest has turned to the use of organic molecules to form such active elements (*e.g.*, memory elements) (*see, e.g.*, U.S. Patents, 6,272,038, 6,212,093, and

6,208,553, and PCT Publication WO 01/03126) and/or to form components of certain devices (e.g., field effect transistors, gates, sensors, transducers, etc.).

[0006] Organic molecules covalently attached to silicon are very stable due to the strength of Si-O and Si-C bonds. A number of approaches exist to form a covalent link between silicon and organic molecules (Buriak and Allen (1998) *J. Am. Chem. Soc.*, 120: 1339-1340; Bansal and Lewis (1998) *J. Phys. Chem.* 102: 1067-1070; Zhu *et al.* (1999) *Langmuir* 15: 8147-8154; Coulter *et al.* (2000) *J. Vac. Sci. Technol. A* 18: 1965-1970; Bourkherroub and Wayner (1999) *J. Am. Chem. Soc.* 121: 11513-11515; Cleland *et al.* (1995) *Faraday Commun.*, 91: 4001-4003; Bateman *et al.* (1998) *Angew. Chem. Int. Ed.*, 37: 2683-2685). These approaches include chemical, electrochemical and vapor deposition on a hydrogen-terminated silicon surface.

[0007] Such approaches, however, have typically involved difficult reaction conditions, have been relatively inefficient, have degraded the organic molecule(s), and/or have resulted in the production of fairly toxic materials.

SUMMARY OF THE INVENTION

[0008] This Invention provides a new procedure for attaching molecules to semiconductor surfaces, in particular silicon. The molecules include porphyrins and ferrocenes, which have been previously shown to be attractive candidates for molecular-based information storage. The new attachment procedure is simple, can be completed in short times, requires minimal amounts of material, is compatible with diverse molecular functional groups, and in some instances affords unprecedented attachment motifs. These features greatly enhance the integration of the molecular materials into the processing steps that are needed to create hybrid molecular/semiconductor information storage devices.

[0009] Thus, in one embodiment, this invention provides a method of covalently coupling an organic molecule to a surface of a Group II, III, IV, V, or VI element or to a semiconductor comprising a Group II, III, IV, V, or VI element (more preferably to a material comprising a Group III, IV, or V element, most preferably to a material comprising a Group IV element). The method typically involves providing a heat resistant organic molecule derivatized with an attachment group (or a linker bearing an attachment group); and contacting the derivatized heat resistant organic molecule with a surface of the

Group II, III, IV, V, or VI element or semiconductor comprising the Group II, III, IV, V, or VI element; and heating the surface to a temperature of at least about 200°C, more preferably to a temperature of at least about 300°C, whereby said attachment group forms a covalent bond with the surface. In certain embodiments, the surface is heated to a temperature of at least about 400°C. In certain embodiments, the heat-resistant organic molecule is a redox-active molecule (*e.g.*, a porphyrin, a porphyrinic macrocycle, an expanded porphyrin, a contracted porphyrin, a linear porphyrin polymer, a porphyrinic sandwich coordination complex, a porphyrin array, *etc.*). In certain embodiments, the organic molecule comprises a porphyrinic macrocycle substituted at a β - position or at a meso- position. In certain embodiments, the organic molecule comprises a porphyrinic macrocycle containing at least two porphyrins of equal energies held apart from each other at a spacing less than about 50 Å such that the molecule has an even or odd hole oxidation state. In the latter state, the hole hops between the porphyrins. The odd hole oxidation state is different from and distinguishable from another oxidation state of the porphyrinic macrocycle. A variety of attachment groups can be used including, but not limited to 4-(hydroxymethyl)phenyl, 4-(*S*-acetylthiomethyl)phenyl, 4-(*Se*-acetylselenomethyl)phenyl, 4-(mercaptomethyl)phenyl, 4-(hydroselenomethyl)phenyl, 4-formylphenyl, 4-(bromomethyl)phenyl, 4-vinylphenyl, 4-ethynylphenyl, 4-allylphenyl, 4-[2-(trimethylsilyl)ethynyl]phenyl, 4-[2-(triisopropylsilyl)ethynyl]phenyl, 4-bromophenyl, 4-iodophenyl, 4-hydroxyphenyl, 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl bromo, iodo, hydroxymethyl, *S*-acetylthiomethyl, *Se*-acetylselenomethyl, mercaptomethyl, hydroselenomethyl, formyl, bromomethyl, chloromethyl, ethynyl, vinyl, allyl, 4-[2-(4-(hydroxymethyl)phenyl)ethynyl]phenyl, 4-(ethynyl)biphen-4'-yl, 4-[2-(triisopropylsilyl)ethynyl]biphen-4'-yl, 3,5-diethynylphenyl, 2-bromoethyl, and the like.

The organic molecule derivatized with the attachment group can include, but is not limited to 5-[4-(*S*-acetylthiomethyl)phenyl]-10,15,20-trimesitylporphinatozinc(II), 5-[4-(mercaptomethyl)phenyl]-10,15,20-trimesitylporphinatozinc(II), 5-[4-(hydroxymethyl)phenyl]-10,15,20-trimesitylporphinatozinc(II), 5-[4-(hydroxymethyl)phenyl]-10,15,20-tri-*p*-tolylporphinatozinc(II), 5-(4-allylphenyl)-10,15,20-trimesitylporphinatozinc(II), 5-(4-formylphenyl)-15-phenyl-10,20-di-*p*-tolylporphinatozinc(II), 5-(4-bromomethylphenyl)-10,15,20-trimesitylporphinatozinc(II), 5-(4-ethynylphenyl)-10,15,20-trimesitylporphinatozinc(II), 5-(4-iodophenyl)-10,15,20-

trimesitylporphinatozinc(II), 5-(4-bromophenyl)-10,15,20-tri-*p*-tolylporphinatozinc(II), 5-(4-hydroxyphenyl)-10,15,20-trimesitylporphinatozinc(II), 5,10-bis(4-ethynylphenyl)-15,20-dimesitylporphinatozinc(II), 5-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]-10,20-bis(3,5-di-*tert*-butylphenyl)-15-mesitylporphinatozinc(II), 5-iodo-10,20-bis(3,5-di-*tert*-butylphenyl)-15-mesitylporphinatozinc(II), 5,10-bis(4-iodophenyl)-15,20-dimesitylporphinatozinc(II), 5-[4-(2-(trimethylsilyl)ethynyl)phenyl]-10,15,20-trimesitylporphinatozinc(II), 5,15-bis(4-ethynylphenyl)-10,20-dimesitylporphinatozinc(II), 5,15-bis(4-iodophenyl)-10,20-dimesitylporphinatozinc(II), 5,10,15-tris(4-ethynylphenyl)-20-mesitylporphinatozinc(II), 5,15-bis(4-ethynylphenyl)-10,20-bis(4-*tert*-butylphenyl)porphinatozinc(II), 5,15-bis(4-ethynylphenyl)porphinatozinc(II), 5,15-bis(3-ethynylphenyl)-10,20-dimesitylporphinatozinc(II), 5,10,15,20-tetrakis(4-ethynylphenyl)porphinatozinc(II), 5,10-bis[4-(2-(trimethylsilyl)ethynyl)phenyl]-15,20-dimesitylporphinatozinc(II), 5-(3,5-diethynylphenyl)-10,15,20-trimesitylporphinatozinc(II), 3,7-dibromo-10,20-bis(3,5-di-*tert*-butylphenyl)-15-mesitylporphinatozinc(II), 5-[4-(2-(trimethylsilyl)ethynyl)phenyl]-10,15,20-tri-*p*-tolylporphinatozinc(II), 5-[4-(*Se*-acetylselenomethyl)phenyl]-10,15,20-trimesitylporphinatozinc(II), 5-(4-iodophenyl)-10,20-bis(3,5-di-*tert*-butylphenyl)-15-mesitylporphinatozinc(II), 5,10-bis(4-ethynylphenyl)-15,20-bis(4-*tert*-butylphenyl)porphinatozinc(II), 5,10-bis(4-ethynylbiphen-4'-yl)-15,20-bis(4-*tert*-butylphenyl)porphinatozinc(II), 5-(4-vinylphenyl)-10,15,20-trimesitylporphinatozinc(II), 5-(4-vinylphenyl)-10,15,20-tri-*p*-tolylporphinatozinc(II), 5-(hydroxymethyl)-10,15,20-trimesitylporphinatozinc(II), 5-(4-allylphenyl)-10,15,20-tri-*p*-tolylporphinatozinc(II), 5-(4-allylphenyl)-10,15,20-tri-*p*-tolylporphinatocopper(II), type c triple decker [(*tert*-butyl)₄phthalocyaninato]Eu[(*tert*-butyl)₄phthalocyaninato]Eu[5,15-bis(4-ethynylphenyl)-10,20-bis(4-*tert*-butylphenyl)porphyrin], type c triple decker [(*tert*-butyl)₄phthalocyaninato]Eu[(*tert*-butyl)₄phthalocyaninato]Eu[5-[4-[2-(4-(hydroxymethyl)phenyl)ethynyl]phenyl]-10,15,20-tri-*p*-tolylporphyrin] 5,10-bis[4-(2-(triisopropylsilyl)ethynyl)biphen-4'-yl]-15,20-bis(4-*tert*-butylphenyl)porphinatozinc(II), 5,10-bis[4-(2-(triisopropylsilyl)ethynyl)phenyl]-15,20-bis(4-*tert*-butylphenyl)porphinatozinc(II), and the like. In certain embodiments, the Group III, IV, or V element is a Group IV element or a doped Group IV element (*e.g.*, silicon, germanium, p- or n-doped silicon, p- or n-doped germanium, *etc.*). The surface can be a hydrogen passivated surface.

[0010] In certain embodiments, the contacting comprises selectively applying the organic molecule to certain regions of said surface and not to other regions. The coating step can comprise placing a protective coating on the surface in regions where the organic molecule is not to be attached; contacting the solution with the surface; and removing the protective coating to provide regions of the surface without the organic molecule. The contacting can comprise contact printing of a solution comprising the organic molecule onto said surface. The contacting can comprise inkjet printing a solution comprising the organic molecule onto the surface. The contacting can comprise spraying or dropping a solution comprising the organic molecule onto the surface. The contacting can comprise dipping or coating the surface with a solution comprising the organic molecule and, optionally, etching regions of the surface to remove the organic molecule.

[0011] In another embodiment, this invention provides a surface of a Group II, III, IV, V, or VI element or a surface of a semiconductor comprising a Group II, III, IV, V, or VI element having an organic molecule coupled thereto through a covalent bond, where the organic molecule is coupled to said surface by methods described herein. In certain embodiments, the organic molecule is a redox-active molecule and includes, but is not limited to any of the molecules described herein. Similarly the attachment groups include, but are not limited to any of the attachment groups described herein. In certain embodiments, the Group II, III, IV, V, or VI element, more preferably a Group III, IV, or V, element, still more preferably a Group IV element or a doped Group IV element (*e.g.*, silicon, germanium, doped silicon, doped germanium, *etc.*). In certain embodiments, the surface comprises a surface in a transistor and/or a surface in a memory element.

[0012] This invention also provides a redox-active substrate comprising a Group II, III, IV, V, or VI material having attached thereto a redox-active molecule where the redox-active molecule is covalently attached to said surface through an attachment group; the redox-active molecule is an organic molecule stable at a temperature of at least about 200 °C; and the covalent attachment is not by a silane. In certain embodiments, the redox-active molecule is coupled to the surface through a linker comprising an atom of carbon, oxygen, sulfur, or selenium. In certain embodiments, the organic molecule and/or the attachment groups include, but are not limited to any of the organic molecules and/or attachment groups described herein. In certain embodiments, the Group III, IV, or V element is a Group IV element (*e.g.*, silicon, germanium, *etc.*). In certain embodiments, the surface is a doped

(*e.g.*, p-doped, n-doped, *etc.*) germanium or silicon surface. In certain embodiments, the substrate comprises an electrochemical cell, and/or a plurality of memory elements, and/or one or more integrated circuit elements (*e.g.*, a transistor, a diode, a logic gate, a rectifier, an optronic element, *etc.*). In certain embodiments, the redox-active molecule on the substrate is electrically coupled to a device that reads or sets the oxidation state of that molecule (*e.g.*, a voltammetric device, an amperometric device, a potentiometric device, a coulometric device, impedance spectrometer, *etc.*). In certain embodiments, a redox-active molecule on the substrate is electrically coupled to a sinusoidal voltammeter.

[0013] This invention also provides a method of fabricating an ordered molecular assembly. The method typically involves providing a solution comprising a heat resistant organic molecule derivatized with an attachment group; contacting the solution with a surface comprising a Group III, IV, or V element at a plurality of discrete locations on the surface; and heating the surface to a temperature of at least about 200°C whereby the attachment groups form covalent bonds with the surface at the plurality of discrete locations. In certain embodiments, the surface is heated to a temperature of at least about 300°C, or 400°C.

[0014] Also provided is a kit for coupling an organic molecule to the surface of a type II, III, IV, V, or VI material. The kit typically involves a container containing a heat resistant organic molecule derivatized with an attachment group. In certain embodiments, the kit optionally additionally includes instructional materials teaching coupling the organic molecule to the surface by heating the surface to a temperature of about 200°C or more.

DEFINITIONS

[0015] The term "oxidation" refers to the loss of one or more electrons in an element, compound, or chemical substituent/subunit. In an oxidation reaction, electrons are lost by atoms of the element(s) involved in the reaction. The charge on these atoms must then become more positive. The electrons are lost from the species undergoing oxidation and so electrons appear as products in an oxidation reaction. An oxidation is taking place in the reaction $\text{Fe}^{2+}(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq}) + \text{e}^-$ because electrons are lost from the species being oxidized, $\text{Fe}^{2+}(\text{aq})$, despite the apparent production of electrons as "free" entities in

oxidation reactions. Conversely the term reduction refers to the gain of one or more electrons by an element, compound, or chemical substituent/subunit.

[0016] An "oxidation state" refers to the electrically neutral state or to the state produced by the gain or loss of electrons to an element, compound, or chemical

5 substituent/subunit. In a preferred embodiment, the term "oxidation state" refers to states including the neutral state and any state other than a neutral state caused by the gain or loss of electrons (reduction or oxidation).

[0017] The term "multiple oxidation states" means more than one oxidation state. In preferred embodiments, the oxidation states may reflect the gain of electrons (reduction) or
10 the loss of electrons (oxidation).

[0018] The terms "different and distinguishable" when referring to two or more oxidation states means that the net charge on the entity (atom, molecule, aggregate, subunit, *etc.*) can exist in two different states. The states are said to be "distinguishable" when the difference between the states is greater than thermal energy at room temperature (*e.g.*, 0°C
15 to about 40°C).

[0019] The term "tightly coupled" when used in reference to a subunit of a multi-subunit (*e.g.*, polymeric) storage molecule of this invention refers to positioning of the subunits relative to each other such that oxidation of one subunit alters the oxidation potential(s) of the other subunit. In a preferred embodiment the alteration is sufficient such
20 that the (non-neutral) oxidation state(s) of the second subunit are different and distinguishable from the non-neutral oxidation states of the first subunit. In a preferred embodiment the tight coupling is achieved by a covalent bond (*e.g.*, single, double, triple, *etc.*). However, in certain embodiments, the tight coupling can be through a linker, via an ionic interaction, via a hydrophobic interaction, through coordination of a metal, or by
25 simple mechanical juxtaposition. It is understood that the subunits could be so tightly coupled that the redox processes are those of a single supermolecule.

[0020] The term "electrode" refers to any medium capable of transporting charge (*e.g.*, electrons) to and/or from a storage molecule. Preferred electrodes are metals or conductive organic molecules. The electrodes can be manufactured to virtually any 2-
30 dimensional or 3-dimensional shape (*e.g.*, discrete lines, pads, planes, spheres, cylinders, *etc.*).

[0021] The term "fixed electrode" is intended to reflect the fact that the electrode is essentially stable and unmovable with respect to the storage medium. That is, the electrode and storage medium are arranged in an essentially fixed geometric relationship with each other. It is of course recognized that the relationship alters somewhat due to expansion and contraction of the medium with thermal changes or due to changes in conformation of the molecules comprising the electrode and/or the storage medium. Nevertheless, the overall spatial arrangement remains essentially invariant. In a preferred embodiment this term is intended to exclude systems in which the electrode is a movable "probe" (*e.g.*, a writing or recording "head", an atomic force microscope (AFM) tip, a scanning tunneling microscope (STM) tip, *etc.*).

[0022] The term "working electrode" is used to refer to one or more electrodes that are used to set or read the state of a storage medium and/or storage molecule.

[0023] The term "reference electrode" is used to refer to one or more electrodes that provide a reference (*e.g.*, a particular reference voltage) for measurements recorded from the working electrode. In preferred embodiments, the reference electrodes in a memory device of this invention are at the same potential although in some embodiments this need not be the case.

[0024] The term "electrically coupled" when used with reference to a storage molecule and/or storage medium and electrode refers to an association between that storage medium or molecule and the electrode such that electrons move from the storage medium/molecule to the electrode or from the electrode to the storage medium/molecule and thereby alter the oxidation state of the storage medium/molecule. Electrical coupling can include direct covalent linkage between the storage medium/molecule and the electrode, indirect covalent coupling (*e.g.*, via a linker), direct or indirect ionic bonding between the storage medium/molecule and the electrode, or other bonding (*e.g.*, hydrophobic bonding). In addition, no actual bonding may be required and the storage medium/molecule may simply be contacted with the electrode surface. There also need not necessarily be any contact between the electrode and the storage medium/molecule where the electrode is sufficiently close to the storage medium/molecule to permit electron tunneling between the medium/molecule and the electrode.

[0025] The term "redox-active unit" or "redox-active subunit" refers to a molecule or component of a molecule that is capable of being oxidized or reduced by the application of a suitable voltage.

5 [0026] The term "redox-active" molecule refers to a molecule or component of a molecule that is capable of being oxidized or reduced by the application of a suitable voltage.

[0027] The term "subunit", as used herein, refers to a redox-active component of a molecule.

10 [0028] The term "electrochemical cell" typically refers to a reference electrode, a working electrode, a redox-active molecule (*e.g.*, a storage medium), and, if necessary, some means (*e.g.*, a dielectric) for providing electrical conductivity between the electrodes and/or between the electrodes and the medium. In some embodiments, the dielectric is a component of the storage medium.

15 [0029] The terms "memory element", "memory cell", or "storage cell" refer to an electrochemical cell that can be used for the storage of information. Preferred "storage cells" are discrete regions of storage medium addressed by at least one and preferably by two electrodes (*e.g.*, a working electrode and a reference electrode). The storage cells can be individually addressed (*e.g.*, a unique electrode is associated with each memory element) or, particularly where the oxidation states of different memory elements are distinguishable,
20 multiple memory elements can be addressed by a single electrode. The memory element can optionally include a dielectric (*e.g.*, a dielectric impregnated with counterions).

[0030] The term "storage location" refers to a discrete domain or area in which a storage medium is disposed. When addressed with one or more electrodes, the storage location may form a storage cell. However if two storage locations contain the same
25 storage media so that they have essentially the same oxidation states, and both storage locations are commonly addressed, they may form one functional storage cell.

[0031] "Addressing" a particular element refers to associating (*e.g.*, electrically coupling) that memory element with an electrode such that the electrode can be used to specifically determine the oxidation state(s) of that memory element.

[0032] The terms "read" or "interrogate" refer to the determination of the oxidation state(s) of one or more molecules (*e.g.*, molecules comprising a storage medium).

[0033] The phrase "output of an integrated circuit" refers to a voltage or signal produced by a one or more integrated circuit(s) and/or one or more components of an
5 integrated circuit.

[0034] A "voltammetric device" is a device capable of measuring the current produced in an electrochemical cell as a result of the application of a voltage or change in voltage.

[0035] An "amperometric device" is a device capable of measuring the current
10 produced in an electrochemical cell as a result of the application of a specific potential field potential ("voltage").

[0036] A "potentiometric device" is a device capable of measuring potential across an interface that results from a difference in the equilibrium concentrations of redox molecules in an electrochemical cell.

15 [0037] A "coulometric device" is a device capable of the net charge produced during the application of a potential field ("voltage") to an electrochemical cell.

[0038] An "impedance spectrometer" is a device capable of determining the overall impedance of an electrochemical cell.

[0039] A "sinusoidal voltammeter" is a voltammetric device capable of determining
20 the frequency domain properties of an electrochemical cell.

[0040] The term "porphyrinic macrocycle" refers to a porphyrin or porphyrin derivative. Such derivatives include porphyrins with extra rings ortho-fused, or ortho-perifused, to the porphyrin nucleus, porphyrins having a replacement of one or more carbon atoms of the porphyrin ring by an atom of another element (skeletal replacement),
25 derivatives having a replacement of a nitrogen atom of the porphyrin ring by an atom of another element (skeletal replacement of nitrogen), derivatives having substituents other than hydrogen located at the peripheral (*meso*-, β -) or core atoms of the porphyrin, derivatives with saturation of one or more bonds of the porphyrin (hydroporphyrins, *e.g.*, chlorins, bacteriochlorins, isobacteriochlorins, decahydroporphyrins, corphins,
30 pyrrocorphins, *etc.*), derivatives obtained by coordination of one or more metals to one or

more porphyrin atoms (metalloporphyrins), derivatives having one or more atoms, including pyrrolic and pyrromethenyl units, inserted in the porphyrin ring (expanded porphyrins), derivatives having one or more groups removed from the porphyrin ring (contracted porphyrins, *e.g.*, corrin, corrole) and combinations of the foregoing derivatives (*e.g.*,
 5 phthalocyanines, sub-phthalocyanines, and porphyrin isomers). Preferred porphyrinic macrocycles comprise at least one 5-membered ring.

[0041] The term "porphyrin" refers to a cyclic structure typically composed of four pyrrole rings together with four nitrogen atoms and two replaceable hydrogens for which various metal atoms can readily be substituted. A typical porphyrin is hemin.

10 [0042] The term "multiporphyrin array" refers to a discrete number of two or more covalently-linked porphyrinic macrocycles. The multiporphyrin arrays can be linear, cyclic, or branched.

[0043] The terms "sandwich coordination compound" or "sandwich coordination complex" refer to a compound of the formula L^nM^{n-1} , where each L is a heterocyclic ligand
 15 (as described below), each M is a metal, n is 2 or more, most preferably 2 or 3, and each metal is positioned between a pair of ligands and bonded to one or more hetero atom (and typically a plurality of hetero atoms, *e.g.*, 2, 3, 4, 5) in each ligand (depending upon the oxidation state of the metal). Thus sandwich coordination compounds are not organometallic compounds such as ferrocene, in which the metal is bonded to carbon atoms.
 20 The ligands in the sandwich coordination compound are generally arranged in a stacked orientation (*i.e.*, are generally cofacially oriented and axially aligned with one another, although they may or may not be rotated about that axis with respect to one another) (*see, e.g.*, Ng and Jiang (1997) *Chemical Society Reviews* 26: 433-442). Sandwich coordination complexes include, but are not limited to "double-decker sandwich coordination compound"
 25 and "triple-decker sandwich coordination compounds". The synthesis and use of sandwich coordination compounds is described in detail in U.S. Patent 6,212,093B1.

[0044] The term "double-decker sandwich coordination compound" refers to a sandwich coordination compound as described above where n is 2, thus having the formula $L^1-M^1-L^2$, wherein each of L^1 and L^2 may be the same or different (*see, e.g.*, Jiang *et al.*
 30 (1999) *J. Porphyrins Phthalocyanines* 3: 322-328).

[0045] The term "triple-decker sandwich coordination compound" refers to a sandwich coordination compound as described above where n is 3, thus having the formula $L^1--M^1--L^2--M^2--L^3$, wherein each of L^1 , L^2 and L^3 may be the same or different, and M^1 and M^2 may be the same or different (*see, e.g., Arnold et al. (1999) Chemistry Letters 483-484*).

[0046] A "linker" is a molecule used to couple two different molecules, two subunits of a molecule, or a molecule to a substrate.

[0047] A "substrate" is a, preferably solid, material suitable for the attachment of one or more molecules. Substrates can be formed of materials including, but not limited to glass, plastic, silicon, germanium, minerals (*e.g., quartz*), semiconducting materials (*e.g., doped silicon, doped germanium, etc.*), ceramics, metals, *etc.*

[0048] In preferred embodiments, when a metal is designated by " M " or " M^n ", where n is an integer, it is recognized that the metal may be associated with a counterion.

[0049] A "group II, III, IV, V, or VI element or material" includes the pure element, a doped variant of the group II, III, IV, V, or VI element and/or an oxidized variant of the group II, III, IV, V or VI element.

[0050] The term "heat-resistant organic molecule" or "heat-stable organic molecule" refers to organic molecules (*e.g., porphyrins*) that are stable (*e.g., show no decomposition, or substantially no decomposition*) at temperature of 200°C to 400°C, preferably at 400°C for at least 30 seconds, preferably for at least one minute, more preferably for at least 2 to 5 minutes.

[0051] A "group III, IV, or V substrate" is a material comprising a Group III, IV, or V element.

[0052] A "a solution comprising a heat resistant organic molecule" is not limited to a true solution, but also includes suspensions, dispersions, and emulsions thereof. In addition, the solution contemplates pastes, gels, aerogels, and essentially any medium suitable for "containing" the heat resistant organic molecule(s).

BRIEF DESCRIPTION OF THE DRAWINGS

[0053] Figure 1 shows illustrative heat-resistant organic molecules for use in the methods of this invention.

5 [0054] Figure 2 illustrates the optimization of concentration of porphyrin alcohol (porphyrin-OH) in THF for attachment of the porphyrin to patterned Si-H surfaces.

[0055] Figure 3 illustrates the effect of baking time of attachment of porphyrin-OH (compound 104) on Si-H using casting and baking process. Other conditions: 400°C, 1 mM in THF, 100 V/s.

10 [0056] Figure 4 illustrates the optimization of baking temperature for attaching porphyrin alcohol (porphyrin-OH) to patterned Si-H surfaces. Other conditions: 1 mM in THF, 60 minutes, 100 V/s.

[0057] Figure 5A shows the cyclic voltammetric behavior of a porphyrin monolayer tethered to Si(100) via a Si-O-C linkage, while Figure 5B shows the integrated voltammetric signal (corresponding to the charge in the monolayer) plotted as a function of
15 the number of cycles.

DETAILED DESCRIPTION

I. Coupling an organic molecule to a substrate.

[0058] This invention pertains to a novel approach to covalently attach organic molecules to a surface of a type II, III, IV, V, or VI material, a doped variant thereof and/or
20 an oxide thereof. In general the method involves: 1) providing a heat resistant organic molecule comprising an attachment group and/or derivatized with an attachment group; and 2) contacting the derivatized heat resistant organic molecule a surface comprising a Group II, III, IV, V, or VI material; and 3) heating the surface and/or molecule to a temperature of at least about 200°C whereby the attachment group forms a covalent bond with the surface.

25 [0059] In certain embodiments, the heat resistant organic molecule is dissolved in an organic solvent (*e.g.*, THF, mesitylene, durene, *o*-dichlorobenzene, 1,2,4-trichlorobenzene, 1-chloronaphthalene, 2-chloronaphthalene, *N,N*-dimethylformamide, *N,N*-dimethylacetamide, *N,N*-dimethylpropionamide, benzonitrile, anisole, and the like). The solvent containing the molecule can then be applied to the surface. Heating can be

accomplished by any of a variety of conventional methods. For example, the solvent can be heated before application to the surface. In certain embodiments, both the solvent and the surface can be heated before the solvent is applied to the surface. In certain preferred embodiments, the surface is heated after application of the solvent. This is conveniently accomplished by baking the surface (*e.g.*, in an oven). In certain preferred embodiments, the surface is heated (*e.g.*, baked) under an inert atmosphere (*e.g.*, argon or other inert gas(es)).

[0060] Various parameters can be optimized for attachment of any particular organic molecule. These include (1) the concentration of the molecule(s), (2) the baking time, and (3) the baking temperature. Figures 2, 3, and 4 show the results of these studies for a representative porphyrin (molecule 104 in Figure 1). In each figure, the left panel shows the cyclic voltammogram of the covalently attached molecule. The characteristic features of the voltammograms are indicative of covalent attachment and robust electrochemical behavior (*see, e.g.*, Li *et al.* (2002 *Appl. Phys. Lett.* 81: 1494-1496; Roth *et al.* (2003) *J. Am. Chem. Soc.* 125: 505-517). The right panel shows the molecular coverage. Saturating coverage for this type of molecule is in the range of 10^{-10} mol cm⁻². Although the three parameters above are not independent, the figures illustrate the following key observations. First, using the methods described herein, the molecules can be attached at relatively high surface coverage (in the range of 5×10^{-11} mol cm⁻²) using micromolar concentrations of materials (*see, e.g.*, Figure 2). Facile attachment using extremely small amounts of material (*e.g.*, concentration less than about 5 mM, preferably less than about 1 mM, more preferably less than about 500 μ M or 100 μ M, still more preferably less than about 10 μ M, and most preferably less than about 1 μ M) is distinctly different from other procedures that have been used to anchor molecules to silicon. These procedures typically use very high concentrations of molecules in solution or neat molecules. The use of very small amounts of material indicates that a few grams of information storage molecules could be used to make millions of chips. The use of small amounts of material also indicates that relatively small amounts of organic solvents can be used, thereby minimizing environmental hazards.

[0061] In addition, it was a surprising discovery that baking times as short as a few minutes (*e.g.*, typically from about 1 sec to about 1 hr, preferably from about 10 sec to about 30 min, more preferably from about 1 minute to about 5, 10, or 15 minutes, and most

preferably from about 30 sec to about 1 or 2 minutes) afford high surface coverage (Figure 3). Short times minimize the amount of energy that is used in the processing step.

[0062] It was also a surprising discovery that baking temperatures as high as 400 °C can be used with no degradation of the molecules (Figure 4). This result is of importance in that many processing steps in fabricating CMOS devices entail high temperature processing. In certain embodiments, preferred baking temperatures range from about 125°C to about 400°C, preferably from about 200°C to about 400°C, more preferably from about 250°C to about 400°C, and most preferably from about 300°C to about 400°C.

[0063] A further significant point is that diverse functional groups on the information storage molecules are suitable for use in attachment to silicon or other substrates. The groups include, but are not limited to, alcohol, thiol, *S*-acetylthiol, bromomethyl, allyl, iodoaryl, carboxaldehyde, ethyne, vinyl, hydroxymethyl. It is also noted that such groups such as ethyl, methyl, or arene afforded essentially no attachment as demonstrated by the failure to achieve substantial attachment with the zinc chelates of octaethylporphyrin, *meso*-tetraphenylporphyrin, *meso*-tetra-*p*-tolylporphyrin, and *meso*-tetramesitylporphyrin.

[0064] The successful attachment via *S*-acetylthiol, bromomethyl, iodoaryl, carboxaldehyde, and ethyne is unprecedented. The successful attachment via the iodoaryl group is extraordinarily valuable in affording a direct aryl-Si attachment. The resulting information-storage molecules can be positioned vertically from the surface, which facilitates subsequent patterning. The ability to attach via such diverse functional groups provides great versatility.

[0065] While in certain embodiments, heating is accomplished by placing the substrate in an oven, essentially any convenient heating method can be utilized, and appropriate heating and contacting methods can be optimized for particular (*e.g.*, industrial) production contexts. Thus, for example, in certain embodiments, heating can be accomplished by dipping the surface in a hot solution containing the organic molecules that are to be attached. Local heating/patterning can be accomplished using for example a hot contact printer, or a laser. Heating can also be accomplished using forced air, a convection oven, radiant heating, and the like. The foregoing embodiments, are intended to be illustrative rather than limiting.

II. The organic molecules.

[0066] It was a surprising discovery that a large number of organic molecules, including redox-active organic molecules, are sufficiently heat resistant to be amenable and even quite effective in the methods of this invention. Suitable heat resistant organic molecules typically include, but are not limited to metallocenes (*e.g.*, ferrocene), porphyrins, expanded porphyrins, contracted porphyrins, linear porphyrin polymers, porphyrin sandwich coordination complexes, and porphyrin arrays.

[0067] Certain preferred heat resistant organic molecules include, but are not limited to 5-[4-(*S*-acetylthiomethyl)phenyl]-10,15,20-trimesitylporphinatozinc(II), 5-[4-(mercaptomethyl)phenyl]-10,15,20-trimesitylporphinatozinc(II), 5-[4-(hydroxymethyl)phenyl]-10,15,20-trimesitylporphinatozinc(II), 5-[4-(hydroxymethyl)phenyl]-10,15,20-tri-*p*-tolylporphinatozinc(II), 5-(4-allylphenyl)-10,15,20-trimesitylporphinatozinc(II), 5-(4-formylphenyl)-15-phenyl-10,20-di-*p*-tolylporphinatozinc(II), 5-(4-bromomethylphenyl)-10,15,20-trimesitylporphinatozinc(II), 5-(4-ethynylphenyl)-10,15,20-trimesitylporphinatozinc(II), 5-(4-iodophenyl)-10,15,20-trimesitylporphinatozinc(II), 5-(4-bromophenyl)-10,15,20-tri-*p*-tolylporphinatozinc(II), 5-(4-hydroxyphenyl)-10,15,20-trimesitylporphinatozinc(II), 5,10-bis(4-ethynylphenyl)-15,20-dimesitylporphinatozinc(II), 5-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]-10,20-bis(3,5-di-*tert*-butylphenyl)-15-mesitylporphinatozinc(II), 5-iodo-10,20-bis(3,5-di-*tert*-butylphenyl)-15-mesitylporphinatozinc(II), 5,10-bis(4-iodophenyl)-15,20-dimesitylporphinatozinc(II), 5-[4-(2-(trimethylsilyl)ethynyl)phenyl]-10,15,20-trimesitylporphinatozinc(II), 5,15-bis(4-ethynylphenyl)-10,20-dimesitylporphinatozinc(II), 5,15-bis(4-iodophenyl)-10,20-dimesitylporphinatozinc(II), 5,10,15-tris(4-ethynylphenyl)-20-mesitylporphinatozinc(II), 5,15-bis(4-ethynylphenyl)-10,20-bis(4-*tert*-butylphenyl)porphinatozinc(II), 5,15-bis(4-ethynylphenyl)porphinatozinc(II), 5,15-bis(3-ethynylphenyl)-10,20-dimesitylporphinatozinc(II), 5,10,15,20-tetrakis(4-ethynylphenyl)porphinatozinc(II), 5,10-bis[4-(2-(trimethylsilyl)ethynyl)phenyl]-15,20-dimesitylporphinatozinc(II), 5-(3,5-diethynylphenyl)-10,15,20-trimesitylporphinatozinc(II), 3,7-dibromo-10,20-bis(3,5-di-*tert*-butylphenyl)-15-mesitylporphinatozinc(II), 5-[4-(2-(trimethylsilyl)ethynyl)phenyl]-10,15,20-tri-*p*-tolylporphinatozinc(II), 5-[4-(*Se*-acetylselenomethyl)phenyl]-10,15,20-trimesitylporphinatozinc(II), 5-(4-iodophenyl)-10,20-bis(3,5-di-*tert*-butylphenyl)-15-mesitylporphinatozinc(II), 5,10-bis(4-ethynylphenyl)-

15,20-bis(4-*tert*-butylphenyl)porphinatozinc(II), 5,10-bis(4-ethynylbiphen-4'-yl)-15,20-bis(4-*tert*-butylphenyl)porphinatozinc(II), 5-(4-vinylphenyl)-10,15,20-trimesitylporphinatozinc(II), 5-(4-vinylphenyl)-10,15,20-tri-*p*-tolylporphinatozinc(II), 5-(hydroxymethyl)-10,15,20-trimesitylporphinatozinc(II), 5-(4-allylphenyl)-10,15,20-tri-*p*-tolylporphinatozinc(II), 5-(4-allylphenyl)-10,15,20-tri-*p*-tolylporphinatocopper(II), type c triple decker [(*tert*-butyl)₄phthalocyaninato]Eu[(*tert*-butyl)₄phthalocyaninato]Eu[5,15-bis(4-ethynylphenyl)-10,20-bis(4-*tert*-butylphenyl)porphyrin], type c triple decker [(*tert*-butyl)₄phthalocyaninato]Eu[(*tert*-butyl)₄phthalocyaninato]Eu[5-[4-[2-(4-(hydroxymethyl)phenyl)ethynyl]phenyl]-10,15,20-tri-*p*-tolylporphyrin] 5,10-bis[4-(2-(triisopropylsilyl)ethynyl)biphen-4'-yl]-15,20-bis(4-*tert*-butylphenyl)porphinatozinc(II), 5,10-bis[4-(2-(triisopropylsilyl)ethynyl)phenyl]-15,20-bis(4-*tert*-butylphenyl)porphinatozinc(II), and the like.

[0068] The suitability of particular molecules for use in the methods of this invention can readily be determined. The molecule(s) of interest are simply coupled to a surface (*e.g.*, a hydrogen passivated surface) according to the methods of this invention. Then sinusoidal voltammetry can be performed (*e.g.*, as described herein or in U.S. Patents, 6,272,038, 6,212,093, and 6,208,553, PCT Publication WO 01/03126, or by (Roth *et al.* (2000) *Vac. Sci. Technol. B* 18: 2359–2364; Roth *et al.* (2003) *J. Am. Chem. Soc.* 125: 505–517) to evaluate 1) whether or not the molecule(s) coupled to the surface, 2) the degree of coverage (coupling); and 3) whether or not the molecule degraded during the coupling procedure.

[0069] Table 1 illustrates the test results (electrochemical characteristics) of a number of porphyrins examined using the attachment procedure described herein. For those porphyrins that attached a subjective EGFP scale was used to rate their electrochemical behavior.

[0070] Table 1. Electrochemical behavior of porphyrins attached to a silicon substrate according to the methods described herein. All substituents are at the *p*-position, and each compound bears one substituent unless noted otherwise.

cmpd #	Result	Structural element (non-linking units)
16	excellent	ZnP-PhCH ₂ SAc (mesityl)
104	excellent	ZnP-PhCH ₂ OH (mesityl)
115	excellent	ZnP-PhCH ₂ OH (<i>p</i> -tolyl)
132	good	TD-dpe-CH ₂ OH
141	excellent	ZnP-Ph-allyl (mesityl)
153	no attachment	ZnTPP
172	excellent	ZnP-Ph-CHO (<i>p</i> -tolyl; phenyl)
178	excellent	ZnP-PhCH ₂ Br (mesityl)
181	no attachment	ZnTTP
182	no attachment	ZnTMP
183	no attachment	ZnOEP
184	excellent	ZnP-PhCCH (mesityl)
185	good	ZnP-PhI (mesityl)
189	Fair	ZnP-PhBr (<i>p</i> -tolyl)
191	excellent	ZnP-PhOH (mesityl)
192	excellent (polymer)	<i>cis</i> -ZnP-(PhCCH) ₂ (mesityl)
193	Fair	ZnP-Ph-B(OR) ₂ (mesityl; 3,5-di- <i>t</i> -BuPh)
194	Fair	ZnP-I (mesityl; 3,5-di- <i>t</i> -BuPh)
195	good	<i>cis</i> -ZnP-(PhI) ₂ (mesityl)
196	excellent	ZnP-PhCC-TMS (mesityl)
197	excellent (polymer)	<i>trans</i> -ZnP-(PhCCH) ₂ (mesityl)
189	good	<i>trans</i> -ZnP-(PhI) ₂ (mesityl)
199	good (polymer)	ZnP-(PhCCH) ₃ (mesityl)
200	good	<i>trans</i> -ZnP-(PhCCH) ₂ (<i>p</i> - <i>t</i> -BuPh)
201	poor	<i>trans</i> -ZnP-(PhCCH) ₂ (H)
202	good	<i>trans</i> -ZnP- <i>m</i> -(PhCCH) ₂ (mesityl)
204	poor	ZnP-(PhCCH) ₄
205	Fair	TD-(PhCCH) ₂
206	excellent	<i>trans</i> -ZnP-(PhCC-TMS) ₂ (mesityl)

cmpd #	Result	Structural element (non-linking units)
207	good	ZnP-Ph-3,5-(CCH) ₂ (mesityl)
208	poor	ZnP-3,7-Br ₂ (mesityl; 3,5-di- <i>t</i> -BuPh)
209	excellent	ZnP-CC-TMS (<i>p</i> -tolyl)

*ZnP is a zinc porphyrin. TD is a triple-decker lanthanide sandwich coordination compound (*e.g.*, as described in U.S. Patent 6,212,093).

It is noted that the above-described compounds are meant to be illustrative and not limiting. Other suitable compounds can readily be ascertained using routine screening procedures as described herein.

[0071] It is also noted that where certain organic molecules decompose at particular sites at high temperature (*e.g.*, 200°C to 400°C) the "reactive" site can often be derivatized with a stable protecting group. The molecule can be coupled to the surface according to the methods of this invention and the protecting group can then be chemically removed from the organic molecule.

[0072] The organic molecule is typically provided in a solvent, dispersion, emulsion, paste, gel, or the like. Preferred solvents, pastes, gels, emulsions, dispersions, *etc.*, are solvents that can be applied to the Group II, III, IV, V, and/or VI material(s) without substantially degrading that substrate and that solubilize or suspend, but do not degrade the organic molecule(s) that are to be coupled to the substrate. In certain embodiments, preferred solvents include high boiling point solvents (*e.g.*, solvents with an initial boiling point greater than about 130°C, preferably greater than about 150°C, more preferably greater than about 180°C). Such solvents include, but are not limited to benzonitrile, dimethylformamide, zylene, orthodichlorobenzene, and the like.

III. The attachment molecules.

[0073] To effect attachment to the substrate (*e.g.*, a Group II, III, IV, V, or VI element, semiconductor, and/or oxide) the heat resistant organic molecule either bears one or more attachment group(s) (*e.g.*, as substituent(s)) and/or is derivatized so that it is attached directly or through a linker to one or more attachment groups.

[0074] A wide variety of attachment molecules (groups) are suitable for use in the methods of this invention. Such attachment groups include, but are not limited to alcohols,

thiols, *S*-acetylthiols, bromomethyls, allyls, iodoaryls, carboxaldehydes, ethynes, and the like. In certain embodiments, the attachment groups include, but are not limited to 4-(hydroxymethyl)phenyl, 4-(*S*-acetylthiomethyl)phenyl, 4-(*Se*-acetylselenomethyl)phenyl, 4-(mercaptomethyl)phenyl, 4-(hydroselenomethyl)phenyl, 4-formylphenyl, 4-(bromomethyl)phenyl, 4-vinylphenyl, 4-ethynylphenyl, 4-allylphenyl, 4-[2-(trimethylsilyl)ethynyl]phenyl, 4-[2-(triisopropylsilyl)ethynyl]phenyl, 4-bromophenyl, 4-iodophenyl, 4-hydroxyphenyl, 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl, bromo, iodo, hydroxymethyl, *S*-acetylthiomethyl, *Se*-acetylselenomethyl, mercaptomethyl, hydroselenomethyl, formyl, bromomethyl, chloromethyl, ethynyl, vinyl, allyl, 4-[2-(4-(hydroxymethyl)phenyl)ethynyl]phenyl, 4-(ethynyl)biphen-4'-yl, 4-[2-(triisopropylsilyl)ethynyl]biphen-4'-yl, 3,5-diethynylphenyl, 2-bromoethyl, and the like. These attachment groups are meant to be illustrative and not limiting.

[0075] The suitability of other attachment groups can readily be evaluated. A heat resistant organic molecule bearing the attachment group(s) of interest (directly or on a linker) is coupled to a substrate (*e.g.*, hydrogen-passivated Si) according to the methods described herein. The efficacy of attachment can then be evaluated electrochemically, *e.g.*, using sinusoidal voltammetry as described above.

[0076] The attachment groups can be substituent(s) comprising the heat-resistant organic molecule. Alternatively, the organic molecule can be derivatized to covalently link the attachment group(s) thereto either directly or through a linker.

[0077] Means of derivatizing molecules, *e.g.*, with alcohols or thiols are well known to those of skill in the art (*see, e.g.*, Gryko *et al.* (1999) *J. Org. Chem.*, 64: 8635-8647; Smith and March (2001) *March's Advanced Organic Chemistry*, John Wiley & Sons, 5th Edition, *etc.*).

[0078] Where the attachment group comprises an alcohol, in certain embodiments, suitable alcohols include, but are not limited to a primary alcohol, a secondary alcohol, a tertiary alcohol, a benzyl alcohol, and an aryl alcohol (*i.e.*, a phenol). Certain particularly preferred alcohols include, but are not limited to 2 to 10 carbon straight chain alcohols, benzyl alcohol, and phenethyl alcohol.

[0079] When the attachment group comprises a thiol, in certain embodiments, suitable thiols include, but are not limited to a primary thiol, a secondary thiol, a tertiary

thiol, a benzyl thiol, and an aryl thiol. Particularly preferred thiols include, but are not limited to 2 to 10 carbon straight chain thiols, benzyl thiol, and phenethyl thiol.

IV. The substrate.

[0080] The methods of this invention are suitable for covalently coupling organic
5 molecules to essentially any or all Group II, III, IV, V, or VI materials (*e.g.*, Group II, III, IV, V, or VI elements, semiconductors, and/or oxides thereof), more preferably to essentially any or all Group III, IV, or V materials (*e.g.*, carbon, silicon, germanium, tin, lead), doped Group II, III, IV, V, and VI elements, or oxides of pure or doped Group II, III, IV, V, or VI elements. In certain preferred embodiments the surface is Group III, IV, or V
10 material, more preferably a Group IV material (oxide, and/or doped variant), still more preferably a silicon or germanium surface or a doped and/or oxidized silicon or germanium surface.

[0081] The group II, III, IV, V, or VI element can be essentially pure, or it can be doped (*e.g.*, p- or n-doped). P- and n-dopants for use with Group II-VI elements, in
15 particular for use with Groups III, IV, and V elements, more particularly for use with Group IV elements (*e.g.*, silicon, germanium, *etc.*) are well known to those of skill in the art. Such dopants include, but are not limited to phosphorous compounds, boron compounds, arsenic compounds, aluminum compounds, and the like. Many doped Group II, III, IV, V, or VI elements are semiconductors and include, but are not limited to ZnS, ZnSe, ZnTe, CdS, CdSe, CdTe, MgS, MgSe, MgTe, CaS, CaSe, CaTe, SrS, SrSe, SrTe, BaS, BaSe, BaTe,
20 GaN, GaP, GaAs, GaSb, InP, InAs, InSb, AlS, AlP, AlSb, PbS, PbSe, Ge and Si and ternary and quaternary mixtures thereof.

[0082] The surface can take essentially any form. For example, it can be provided as a planar substrate, an etched substrate, a deposited domain on another substrate and the
25 like. Particularly preferred forms include those forms of common use in solid state electronics fabrication processes.

[0083] Although not necessarily required, in certain embodiments the surface is cleaned before use, *e.g.*, using standard methods known to those of skill in the art. Thus, for example, in one preferred embodiment, the surface can be cleaned by sonication in a series
30 of solvents (*e.g.*, acetone, toluene, acetone, ethanol, and water) and then exposed to a

standard wafer-cleaning solution (*e.g.*, Piranha (sulfuric acid: 30% hydrogen peroxide, 2:1)) at an elevated temperature (*e.g.*, 100°C).

[0084] In certain embodiments, oxides can be removed from the substrate surface and the surface can be hydrogen passivated. A number of approaches to hydrogen passivation are well known to those of skill in the art. For example, in one approach, a flow of molecular hydrogen is passed through dense microwave plasma across a magnetic field. The magnetic field serves to protect the sample surface from being bombarded by charged particles. Hence the crossed beam (CB) method makes it possible to avoid plasma etching and heavy ion bombardment that are so detrimental for many semiconductor devices (*see, e.g.*, Balmashnov, *et al.* (1990) *Semiconductor Science and Technology*, 5: 242). In one particularly preferred embodiment, passivation is by contacting the surface to be passivated with an ammonium fluoride solution (preferably sparged of oxygen).

[0085] Other methods of cleaning and passivating surfaces are known to those of skill in the art (*see, e.g.*, Choudhury (1997) *The Handbook of Microlithography, Micromachining, and Microfabrication*, Soc. Photo-Optical Instru. Engineer, Bard & Faulkner (1997) *Fundamentals of Microfabrication*, and the like).

V. Patterning the Organic Molecule(s) on the substrate

[0086] In certain embodiments, the heat-resistant organic molecules are attached to form a uniform film across the surface of the Group II, III, IV, V, or VI material. In other embodiments, the organic molecules are separately coupled at one or more discrete locations on the surface. In certain embodiments, different molecules are coupled at different locations on the surface.

[0087] The location at which the molecules are coupled can be accomplished by any of a number of means. For example, in certain embodiments, the solution(s) comprising the organic molecule(s) can be selectively deposited at particular locations on the surface. In certain other embodiments, the solution can be uniformly deposited on the surface and selective domains can be heated. In certain embodiments, the organic molecules can be coupled to the entire surface and then selectively etched away from certain areas.

[0088] The most common approach to selectively contacting the surface with the organic molecule(s) involves masking the areas of the surface that are to be free of the

organic molecules so that the solution containing the molecule(s) cannot come in contact with those areas. This is readily accomplished by coating the substrate with a masking material (*e.g.*, a polymer resist) and selectively etching the resist off of areas that are to be coupled. Alternatively a photoactivatable resist can be applied to the surface and selectively activated (*e.g.*, via UV light) in areas that are to be protected. Such "photolithographic" methods are well known in the semiconductor industry (*see e.g.*, Van Zant (2000) *Microchip Fabrication: A Practical Guide to Semiconductor Processing*; Nishi and Doering (2000) *Handbook of Semiconductor Manufacturing Technology*; Xiao (2000) *Introduction to Semiconductor Manufacturing Technology*; Campbell (1996) *The Science and Engineering of Microelectronic Fabrication (Oxford Series in Electrical Engineering)*, Oxford University Press, and the like). In addition, the resist can be patterned on the surface simply by contact printing the resist onto the surface.

[0089] Other approaches involve contact printing of the reagents, *e.g.*, using a contact printhead shaped to selectively deposit the reagent(s) in regions that are to be coupled, use of an inkjet apparatus (*see e.g.*, U.S. Patent 6,221,653) to selectively deposit reagents in particular areas, use of dams to selectively confine reagents to particular regions, and the like.

[0090] In certain preferred embodiments, the coupling reaction is repeated several times. After the reaction(s) are complete, uncoupled organic molecules are washed off of the surface, *e.g.*, using standard wash steps (*e.g.*, benzonitrile wash followed by sonication in dry methylene chloride).

[0091] The foregoing methods are intended to be illustrative. In view of the teachings provided herein, other approaches will be evident to those of skill in the semiconductor fabrication arts.

VI. High charge density materials.

[0092] It was a surprising discovery of this invention that coupling of redox-active molecules to a doped or undoped substrate (*e.g.*, a substrate comprising a group III, IV, or V element) results in higher and more uniform packing of the organic molecules (*e.g.*, redox-active species) than other previously known methods. With redox-active organic molecules this manifests as lower oxidative current at higher anodic potentials observed in voltametric

measurements. In addition, a cyclic voltammogram shows sharper and more symmetric peaks.

[0093] In addition, the improved uniformity and higher packing density of redox-active molecules on the substrate results in materials capable of storing a significantly higher charge density. Thus, in preferred embodiments, this invention provides a group IV element substrate having coupled thereto one or more redox-active species that can store charge at a charge density of at least about 75 $\mu\text{Coulombs}/\text{cm}^2$, preferably at least about 100 $\mu\text{Coulombs}/\text{cm}^2$, more preferably at least about 150 $\mu\text{Coulombs}/\text{cm}^2$, and most preferably of at least about 200 or 250 $\mu\text{Coulombs}/\text{cm}^2$ per non-zero oxidation state of the redox-active molecules. Such materials are useful in the fabrication of molecular memories (memory chips).

[0094] Where various binding moieties are used instead of redox-active species, the high uniformity and molecule density provides sensors having greater sensitivity and selectivity for a particular analyte.

VII. Uses of organic molecules coupled to a Group IV material.

[0095] The methods of this invention can be used to attach essentially any heat-resistant organic molecule to a Group II, III, IV, V, or VI material surface, preferably to a Group III, IV, or V surface. In certain preferred embodiments, the molecule is a redox-active molecule and can be used to form a molecular memory. In other preferred embodiments, the molecule can be essentially any other heat-resistant molecule. Certain other heat-resistant molecules include, but are not limited to binding partner (*e.g.*, certain antibodies, ligands, nucleic acids, sugars, *etc.*) and can be used to form a sensor for detecting particular analyte(s).

[0096] In "molecular memory" redox-active molecules (molecules having one or more non-zero redox states) coupled to the Group II, III, IV, V, or VI materials are used to store bits (*e.g.*, each redox state can represent a bit). The redox-active molecule attached to the substrate material (*e.g.*, silicon, germanium, *etc.*) forms a storage cell capable of storing one or more bits in various oxidation states. In certain embodiments, the storage cell is characterized by a fixed electrode electrically coupled to a "storage medium" comprising one or more redox-active molecules and having a multiplicity of different and

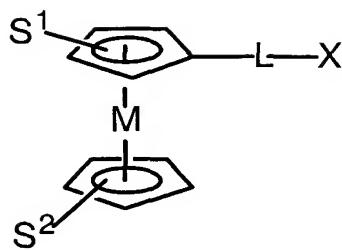
distinguishable oxidation states. Data is stored in the (preferably non-neutral) oxidation states by the addition or withdrawal of one or more electrons from said storage medium via the electrically coupled electrode. The oxidation state of the redox-active molecule(s) can be set and/or read using electrochemical methods (*e.g.*, cyclic voltammetry), *e.g.*, as
5 described in U.S. Patents, 6,272,038, 6,212,093, and 6,208,553 and PCT Publication WO 01/03126.

[0097] Because group II, III, IV, V, and VI materials, in particular group IV materials (*e.g.*, silicon, germanium, *etc.*), are commonly used in electronic chip fabrication, the methods provided herein readily lend themselves to the fabrication of molecular
10 memory chips compatible with existing processing/fabrication technologies. In addition, details on the construction and use of storage cells comprising redox-active molecules can be found, in U.S. Patents, 6,272,038, 6,212,093, and 6,208,553 and PCT Publication WO 01/03126.

[0098] Certain preferred redox-active molecules suitable for use in this invention are
15 characterized by having a multiplicity of oxidation states. Those oxidation states are provided by one or more redox-active units. A redox-active unit refers to a molecule or to a subunit of a molecule that has one or more discrete oxidation states that can be set by application of an appropriate voltage. Thus, for example, in one embodiment, the redox-active molecule can comprise two or more (*e.g.*, 8) different and distinguishable oxidation
20 states. Typically, but not necessarily, such multi-state molecules will be composed of several redox-active units (*e.g.*, porphyrins or ferrocenes). Each redox-active molecule is itself at least one redox-active unit, or comprises at least one redox-active unit, but can easily comprise two or more redox-active units.

[0099] Preferred redox-active molecules include, but are not limited to porphyrinic
25 macrocycles. Particularly preferred redox-active molecules include a porphyrin, an expanded porphyrin, a contracted porphyrin, a ferrocene, a linear porphyrin polymer, a porphyrin sandwich coordination complex, and a porphyrin array.

[0100] In certain embodiments, the redox-active molecule is a metallocene as shown in Formula I.

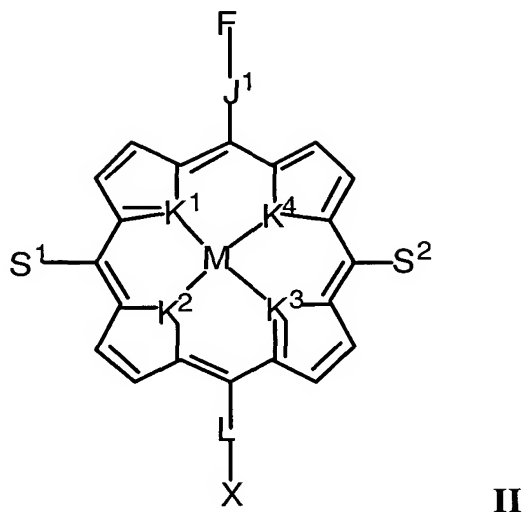


where L is a linker, M is a metal (*e.g.*, Fe, Ru, Os, Co, Ni, Ti, Nb, Mn, Re, V, Cr, W), S¹ and S² are substituents independently selected from the group consisting of aryl, phenyl, cycloalkyl, alkyl, halogen, alkoxy, alkylthio, perfluoroalkyl, perfluoroaryl, pyridyl, cyano, thiocyanato, nitro, amino, alkylamino, acyl, sulfoxyl, sulfonyl, imido, amido, and carbamoyl. In preferred embodiments, a substituted aryl group is attached to the porphyrin, and the substituents on the aryl group are selected from the group consisting of aryl, phenyl, cycloalkyl, alkyl, halogen, alkoxy, alkylthio, perfluoroalkyl, perfluoroaryl, pyridyl, cyano, thiocyanato, nitro, amino, alkylamino, acyl, sulfoxyl, sulfonyl, imido, amido, and carbamoyl.

[0101] Certain suitable substituents include, but are not limited to, 4-chlorophenyl, 3-acetamidophenyl, 2,6-dichloro-4-trifluoromethyl, and the like. Preferred substituents provide a redox potential range of less than about 2 volts. X is selected from the group consisting of a substrate, a reactive site that can covalently couple to a substrate (*e.g.*, an alcohol, a thiol, *etc.*). It will be appreciated that in some embodiments, L-X is an alcohol or a thiol. In certain instances L-X can be replaced with another substituent (S³) like S¹ or S². In certain embodiments, L-X can be present or absent, and when present preferably is 4-hydroxyphenyl, 4-(2-(4-hydroxyphenyl)ethynyl)phenyl, 4-(hydroxymethyl)phenyl, 4-mercaptophenyl, 4-(2-(4-mercaptophenyl)ethynyl)phenyl, 4-mercaptomethylphenyl, 4-hydroselenophenyl, 4-(2-(4-hydroselenophenyl)ethynyl)phenyl, 4-hydrotelluorophenyl, 4-(hydroselenomethyl)phenyl, 4-(2-(4-hydrotelluorophenyl)ethynyl)phenyl, 4-(hydrotelluromethyl)phenyl, and the like.

[0102] The oxidation state of molecules of Formula **I** is determined by the metal and the substituents. Various suitable metallocenes are disclosed in U.S. Patents, 6,272,038, 6,212,093, and 6,208,553, and PCT Publication WO 01/03126.

[0103] Other suitable redox-active molecules include, but are not limited to porphyrins illustrated by Formula II.



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where, F is a redox-active subunit (*e.g.*, a ferrocene, a substituted ferrocene, a metalloporphyrin, or a metallochlorin, *etc.*), J¹ is a linker, M is a metal (*e.g.*, Zn, Mg, Cd, Hg, Cu, Ag, Au, Ni, Pd, Pt, Co, Rh, Ir, Mn, B, Al, Ga, Pb, and Sn), S¹ and S² are independently selected from the group consisting of aryl, phenyl, cycloalkyl, alkyl, halogen, alkoxy, alkylthio, perfluoroalkyl, perfluoroaryl, pyridyl, cyano, thiocyanato, nitro, amino, alkylamino, acyl, sulfoxyl, sulfonyl, imido, amido, and carbamoyl wherein said substituents provide a redox potential range of less than about 2 volts, K¹, K², K³, and K⁴ are independently selected from the group consisting of N, O, S, Se, Te, and CH; L is a linker; X is selected from the group consisting of a substrate, a reactive site that can covalently couple to a substrate. In preferred embodiments, X or L-X is an alcohol or a thiol. In some embodiments L-X can be eliminated and replaced with a substituent independently selected from the same group as S¹ or S².

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[0104] Other suitable molecules include, but are not limited to 5-[4-(S-acetylthiomethyl)phenyl]-10,15,20-trimesitylporphinatozinc(II), 5-[4-(mercaptomethyl)phenyl]-10,15,20-trimesitylporphinatozinc(II), 5-[4-(hydroxymethyl)phenyl]-10,15,20-trimesitylporphinatozinc(II), 5-[4-(hydroxymethyl)phenyl]-10,15,20-tri-*p*-tolylporphinatozinc(II), 5-(4-allylphenyl)-10,15,20-trimesitylporphinatozinc(II), 5-(4-formylphenyl)-15-phenyl-10,20-di-*p*-

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tolylporphinatozinc(II), 5-(4-bromomethylphenyl)-10,15,20-trimesitylporphinatozinc(II),
 5-(4-ethynylphenyl)-10,15,20-trimesitylporphinatozinc(II), 5-(4-iodophenyl)-10,15,20-
 trimesitylporphinatozinc(II), 5-(4-bromophenyl)-10,15,20-tri-*p*-tolylporphinatozinc(II), 5-
 (4-hydroxyphenyl)-10,15,20-trimesitylporphinatozinc(II), 5,10-bis(4-ethynylphenyl)-15,20-
 5 dimesitylporphinatozinc(II), 5-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]-
 10,20-bis(3,5-di-*tert*-butylphenyl)-15-mesitylporphinatozinc(II), 5-iodo-10,20-bis(3,5-di-
tert-butylphenyl)-15-mesitylporphinatozinc(II), 5,10-bis(4-iodophenyl)-15,20-
 dimesitylporphinatozinc(II), 5-[4-(2-(trimethylsilyl)ethynyl)phenyl]-10,15,20-
 trimesitylporphinatozinc(II), 5,15-bis(4-ethynylphenyl)-10,20-dimesitylporphinatozinc(II),
 10 5,15-bis(4-iodophenyl)-10,20-dimesitylporphinatozinc(II), 5,10,15-tris(4-ethynylphenyl)-
 20-mesitylporphinatozinc(II), 5,15-bis(4-ethynylphenyl)-10,20-bis(4-*tert*-
 butylphenyl)porphinatozinc(II), 5,15-bis(4-ethynylphenyl)porphinatozinc(II), 5,15-bis(3-
 ethynylphenyl)-10,20-dimesitylporphinatozinc(II), 5,10,15,20-tetrakis(4-
 ethynylphenyl)porphinatozinc(II), 5,10-bis[4-(2-(trimethylsilyl)ethynyl)phenyl]-15,20-
 15 dimesitylporphinatozinc(II), 5-(3,5-diethynylphenyl)-10,15,20-trimesitylporphinatozinc(II),
 3,7-dibromo-10,20-bis(3,5-di-*tert*-butylphenyl)-15-mesitylporphinatozinc(II), 5-[4-(2-
 (trimethylsilyl)ethynyl)phenyl]-10,15,20-tri-*p*-tolylporphinatozinc(II), 5-[4-(*Se*-
 acetylselenomethyl)phenyl]-10,15,20-trimesitylporphinatozinc(II), 5-(4-iodophenyl)-10,20-
 bis(3,5-di-*tert*-butylphenyl)-15-mesitylporphinatozinc(II), 5,10-bis(4-ethynylphenyl)-
 20 15,20-bis(4-*tert*-butylphenyl)porphinatozinc(II), 5,10-bis(4-ethynylbiphen-4'-yl)-15,20-
 bis(4-*tert*-butylphenyl)porphinatozinc(II), 5-(4-vinylphenyl)-10,15,20-
 trimesitylporphinatozinc(II), 5-(4-vinylphenyl)-10,15,20-tri-*p*-tolylporphinatozinc(II), 5-
 (hydroxymethyl)-10,15,20-trimesitylporphinatozinc(II), 5-(4-allylphenyl)-10,15,20-tri-*p*-
 tolylporphinatozinc(II), 5-(4-allylphenyl)-10,15,20-tri-*p*-tolylporphinatocopper(II), type c
 25 triple decker [(*tert*-butyl)₄phthalocyaninato]Eu[(*tert*-butyl)₄phthalocyaninato]Eu[5,15-bis(4-
 ethynylphenyl)-10,20-bis(4-*tert*-butylphenyl)porphyrin], type c triple decker [(*tert*-
 butyl)₄phthalocyaninato]Eu[(*tert*-butyl)₄phthalocyaninato]Eu[5-[4-[2-(4-
 (hydroxymethyl)phenyl)ethynyl]phenyl]-10,15,20-tri-*p*-tolylporphyrin] 5,10-bis[4-(2-
 (triisopropylsilyl)ethynyl)biphen-4'-yl]-15,20-bis(4-*tert*-butylphenyl)porphinatozinc(II),
 30 5,10-bis[4-(2-(triisopropylsilyl)ethynyl)phenyl]-15,20-bis(4-*tert*-
 butylphenyl)porphinatozinc(II), and the like.

[0105] Control over the hole-storage and hole-hopping properties of the redox-active units of the redox-active molecules used in the memory devices of this invention allows fine control over the architecture of the memory device.

[0106] Such control is exercised through synthetic design. The hole-storage
5 properties depend on the oxidation potential of the redox-active units or subunits that are themselves or that are used to assemble the redox-active storage media used in the devices of this invention. The hole-storage properties and redox potential can be tuned with precision by choice of base molecule(s), associated metals and peripheral substituents (Yang *et al.* (1999) *J. Porphyrins Phthalocyanines*, 3: 117-147). The design of molecules
10 for molecular memory is discussed in detail in U.S. Patents, 6,272,038, 6,212,093, and 6,208,553, and PCT Publication WO 01/03126.

VIII. Kits.

[0107] In still another embodiment, this invention provides kits for practice of the method of this invention or for use of the materials produced by methods of this invention.
15 In one embodiment, the kit comprises one or more reagents used to couple an organic molecule to a type II, III, IV, V, or VI material according to the methods of this invention. Such reagents include, but are not limited to reagents for cleaning and/or passivating the material surface, and/or the organic molecule(s) that are to be coupled to the surface, and/or attachment molecules for derivatizing the organic molecule(s) (*e.g.*, reagents for
20 derivatizing an organic molecule with an alcohol or a thiol), and/or solvents for use in coupling the derivatized organic molecule to the surface, and/or reagents for washing the derivatized surface, and the like

[0108] In certain embodiments, the kits comprise a type II, III, IV, V, or VI material having a heat-resistant organic molecule (*e.g.*, a redox-active molecule) coupled thereto as
25 described herein. The type II, III, IV, V, or VI material can, in certain embodiments, comprise a molecular memory and in, certain embodiments, comprise a sensor.

[0109] In addition, the kits can optionally include instructional materials containing directions (*i.e.*, protocols) for the practice of the methods of this invention. Preferred instructional materials provide protocols utilizing the kit contents for coupling a heat-
30 resistant organic molecule to a type II, III, IV, V, or VI material according to the methods of

this invention, and/or for using type II, III, IV, V, or VI materials having coupled organic molecules as memory elements or as sensors. While the instructional materials typically comprise written or printed materials they are not limited to such. Any medium capable of storing such instructions and communicating them to an end user is contemplated by this invention. Such media include, but are not limited to electronic storage media (*e.g.*, magnetic discs, tapes, cartridges, chips), optical media (*e.g.*, CD ROM), and the like. Such media may include addresses to internet sites that provide such instructional materials.

EXAMPLES

[0110] The following examples are offered to illustrate, but not to limit the claimed invention.

Example 1

Molecules Can Perform in Electronic Devices Under Real-World Processing and Operating Conditions.

[0111] The central tenet of the field of molecular electronics is that molecular components can be used as functional elements in place of the semiconductor-based devices present in conventional microcircuitry (Kwok and Ellenbogen (2002) *Materials Today*, 28-37; Carroll and Gorman (2002) *Angew. Chem. Int. Ed.* 41: 4378–4400). To serve in this role, the molecular components should remain robust under daunting conditions including high-temperature (*e.g.*, 400 °C) processing steps during manufacture and very large numbers (10^9 - 10^{12}) of operational cycles over a lifetime (*International Technology Roadmap for Semiconductors (ITRS)*, Semiconductor Industry Association, San Jose, CA (2000)). There has been considerable skepticism whether molecular materials possess adequate stability to meet such requirements. Herein, we demonstrate that porphyrin-based information storage media meet the processing and operating challenges required for use in computational devices.

[0112] Our approach for molecular-based information storage employs redox-active porphyrin molecules as charge-storage elements (Roth *et al.* (2000) *Vac. Sci. Technol. B* 18: 2359–2364). We have shown that these molecules can be covalently attached to device-grade silicon platforms to form the basis of first-generation hybrid molecular/semiconductor devices (Roth *et al.* (2003) *J. Am. Chem. Soc.* 125: 505–517). The porphyrin-based

information storage elements exhibit charge-retention times that are long (minutes) compared with those of the semiconductor elements in dynamic random access memory (milliseconds) (Roth *et al.* (2000) *Vac. Sci. Technol. B* 18: 2359–2364; Roth *et al.* (2003) *J. Am. Chem. Soc.* 125: 505–517). These molecules also exhibit redox characteristics that make them amenable for use as multibit information-storage media.

[0113] Figure 5A shows the cyclic voltammetric behavior of a porphyrin monolayer tethered to Si(100) via a Si-O-C linkage. This monolayer was formed by placing a small amount (~1 μL) of a dilute solution (~100 μM) on a micron-scale photolithographically patterned, hydrogen-passivated Si(100) platform and baking the sample at 400 °C for several minutes under inert atmosphere conditions. The voltammetric response of the porphyrin monolayer is identical to that of porphyrin monolayers formed at much lower temperatures (100–200 °C for several hours) (Roth *et al.* (2003) *J. Am. Chem. Soc.* 125: 505–517) and demonstrates that molecular integrity is maintained at temperatures where most organic molecules thermally decompose. The high-temperature procedure is readily adaptable to current semiconductor fabrication technology and has the important added benefit that extremely small quantities of material are needed to make a device.

[0114] The robustness of the porphyrin information-storage medium was examined by repeatedly performing the cycle of (1) oxidizing the electrically neutral monolayer and (2) reducing the resulting positively charged monolayer to its electrically neutral state. The oxidation event is equivalent to writing a bit of information; the reduction event is equivalent to erasing or destructively reading out the information. The five voltammograms in Figure 5A show the response of the system after 0, 2.5×10^4 , 1.8×10^6 , 1.1×10^9 , and 1.0×10^{10} oxidation/reduction cycles. During the experiment, the nature of the electrical cycling was varied. On some days, the system was continuously cycled for 24 hrs. On others, cycling was stopped intentionally for periods ranging from a few minutes up to 12 hrs. At one point, cycling was stopped unintentionally due to an electrical power failure. The data indicate that after an initial “burn-in” period of $\sim 10^7$ cycles the voltammetric response stabilizes. This robustness of the system is further illustrated in Figure 5B wherein the integrated voltammetric signal (corresponding to the charge in the monolayer) is plotted as a function of the number of cycles. These data indicate that the charge-storage characteristics of the monolayer exhibit minimal variation (few percent) over the course of

the entire experiment. At the time cycling was arbitrarily stopped ($>10^{10}$ cycles; ~27 days), the system showed no signs of degradation. Collectively, these data indicate that the porphyrin-based information storage medium is extremely robust and augur well for the use of selected molecules in hybrid molecular/semiconductor electronic devices.

5 **[0115]** It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to persons skilled in the art and are to be included within the spirit and purview of this application and scope of the appended claims. All publications, patents, and patent applications cited herein are hereby incorporated by reference in their entirety for all
10 purposes.